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PATENT SPECIFICATION

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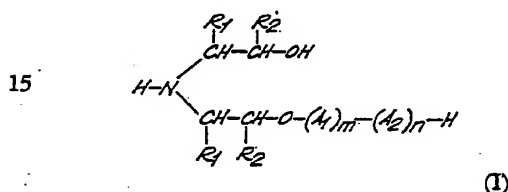
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(54) PROCESS FOR THE PREPARATION OF POLYETHER AMINES

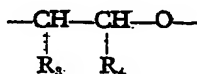
(71) We, BAYER AKTIENGESSELLSCHAFT, a body corporate organised under the laws of Germany, of 509 Leverkusen-Bayerwerk, Germany (Fed. Rep.), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The invention relates to a new process for the preparation of polyether amines; more particularly it concerns a new process for the preparation of secondary polyether amines of the formula



in which

20 R_1 and R_2 , independently of one another, stand for hydrogen, an alkyl or aryl radical, preferably for hydrogen or a C_{1-4} alkyl radical,
 A_1 and A_2 , independently of one another, denote an oxyalkylene group of the formula



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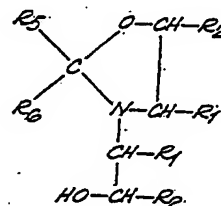
in which

R_3 and R_4 , independently of one another, stand for hydrogen, an alkyl or aryl radical, preferably for hydrogen and a C_{1-4} alkyl radical, and

[Price 33p]

m is a number between 1 and 100, preferably 2 and 30, and
 n is nought or a number between 1 and 100, preferably 2 to 30

which is characterised in that oxazolidines of the formula



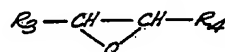
(II)

in which

R_1 and R_2 have the meaning stated under Formula I, and

R_5 and R_6 , independently of one another, stand for hydrogen, an alkyl or aryl group or, together with the C atom, form a 5- or 6-membered cycloalkane ring

are reacted with alkylene oxides of the formula



(III)

in which

R_3 and R_4 have the meaning stated under Formula I and the hydroxyalkylation products formed are hydrolysed.

For R_1 , R_2 , R_3 and R_4 there are men-

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tioned for example: as alkyl radicals; above all, C_{1-4} alkyl radical, for example the methyl, ethyl, n-propyl and butyl radical; as aryl radical, the phenyl radical. For R_3 or R_4 , the chloromethyl radical is also mentioned.

For R_3 and R_4 , there are suitable e.g.: as alkyl radicals; above all, C_{1-4} alkyl radicals, for example the methyl, ethyl, n-propyl, i-propyl and butyl radical; as aryl group, in particular the phenyl group.

The N - β - hydroxyalkyloxazolidines to be used as starting compounds in the process according to the invention are readily obtainable according to processes known per se. They are formed by condensation of aliphatic, cycloaliphatic or aromatic aldehydes or ketones, for example formaldehyde, acetaldehyde, propionaldehyde, n- and i-butyraldehyde, benzaldehyde, acetone, methyl ethyl ketone, methyl propyl ketone, methyl isopropyl ketone, methyl isobutyl ketone, diethyl ketone, diisopropyl ketone, diisobutyl ketone, cyclopentanone or cyclohexanone, with N - 2 - hydroxyalkyl - β - amino - alkanols, for example diethanolamine, bis - (2 - hydroxypropyl) - amine, bis - (2 - hydroxy - 1 - methylpropyl) - amine or bis - (2 - hydroxybutyl) - amine, preferably diethanolamine. The condensation is preferably carried out in inert organic solvents which form an azeotropic mixture with the water formed in the reaction. Such solvents are e.g. toluene, xylene or benzene.

The N - β - hydroxyalkyloxazolidines are, according to the invention, reacted with alkylene oxides, for example ethylene oxide, propylene oxide, 1,2- and 2,3-epoxybutane, 2,3-epoxypentane, styrene oxide or epichlorohydrin. The hydroxyalkylation takes place at temperatures between 40 and 200°C, preferably between 80 and 180°C. The reaction can be carried out at normal pressure; in order to shorten the reaction time it may, however, be advantageous to work at slightly increased pressures, e.g. from 1 to 6 atmospheres. The hydroxyalkylation of the N - β - hydroxyalkyloxazolidines can be carried out both without catalyst and in the presence of the known hydroxyalkylation catalysts. As hydroxyalkylation catalysts, both basic catalysts, for example alkali metal hydroxides and alkaline earth metal hydroxides, alkali metal carbonates and alkaline earth metal carbonates, alkali metal alcoholates, sodium hydride, sodium amide, tertiary amines and quaternary ammonium bases, and acid catalysts, for example iron (III) chloride, boron trifluoride, tin tetrachloride and antimony pentachloride, are suitable. Since, however, in the case of acid catalysis, side-reactions readily occur, basic catalysis is to be preferred. Usually the catalysts are employed in amounts of 0.05 to 2 per cent by weight, referred to the weight of the N - β - hydroxyalkyloxazolidines to be hydroxyalkylated.

To prepare the polyether amines of the formula I, the N - β - hydroxyalkyloxazolidine hydroxyalkylation products are subjected to hydrolysis. There here takes place the splitting of the oxazolidines into the polyether amines according to the invention of the formula I and the aldehydes or ketones on which the N - β - hydroxyalkyloxazolidines are based. The hydrolytic splitting takes place spontaneously upon the addition of at least molar amounts of water to the polyether-substituted oxazolidines; the carbonyl compounds formed can subsequently be distilled off from the polyether amine or can be extracted from it with organic solvents. It is, however, advantageous to carry out the hydrolysis at elevated temperatures and to distil off the carbonyl compounds formed and the excess water from polyether amine. The hydrolytic splitting can be catalysed by addition of catalytic amounts of mineral acids, e.g. hydrochloric or sulphuric acid, but such a catalysis is not necessary. Preferably, the hydrolysis is carried out by blowing superheated steam into the N - β - hydroxyalkyloxazolidine hydroxyalkylation products. Separation of the carbonyl compound formed is, with this method of working, likewise effected with steam. The carbonyl compound can then subsequently be separated by phase separation or extraction from the condensed water and again used for the preparation of N - 2 - hydroxyalkyloxazolidine.

The secondary polyether amines obtainable according to the process of the invention are liquid or waxy, depending on the number and nature of the alkylene oxide units contained in them. Coloured products can be lightened by customary lightening operations, e.g. treatment with active carbon, bleaching earth, sodium hypochlorite, Raney nickel or hydrogen peroxide. The secondary polyether amines are useful as textile auxiliaries and raw materials for detergents furthermore as starting materials for the preparation of polyurethanes.

A process for the preparation of secondary polyether amines of the formula I is described in U.S. Patent Specification 2 629 740. According to this, the compounds are obtained by reaction of N-unsubstituted oxazolidines with alkylene oxides and subsequent hydrolysis of the resultant hydroxyalkylation products to give polyether amines. The preparation of homogeneous secondary polyether amines of the formula I, however, is not possible according to this process since the N-unsubstituted oxazolidines used are in tautomeric equilibrium with the open-chain N - 2 - hydroxyalkylazomethines which, moreover, is shifted in favour of the azomethines by temperature increase (E. D. Bergmann et al, JACS 72, 2866; J. Metzger, Rec. trav. chim. 71, 243) and, therefore, in the alkoxylation, which, as is shown, is carried out at

5 elevated temperatures, there are always obtained mixtures of polyether-substituted azomethines and oxazolidines, the hydrolysis of which again yields mixtures of primary and secondary polyether amines. Compared to this known process, the process according to the invention exhibits the advantage that it renders possible in simple manner the preparation of pure secondary polyether amines.

10

Example 1

39 g (0.2 mole) 3 - β - hydroxyethyl - 2 - phenyloxazolidine, the preparation of which is described hereinafter, are reacted, with stirring, with 55 g (1.25 moles) ethylene

oxide in the presence of 0.2 g of anhydrous sodium hydroxide powder in a nitrogen atmosphere in 5 hours at 150°C. The reaction product is heated under reflux with 100 ml of water for 1 hour. After cooling, the benzaldehyde formed is extracted from the hydrolysis mixture twice with, in each case, 75 ml chloroform. Subsequently, the water is distilled out of the polyether amine solution, first on a rotary evaporator and then in an oil pump vacuum of 1 to 3 mm Hg until the base of the column has a temperature of 130°C. 75 g of the secondary polyether amine of the formula



30 are obtained in the form of a water-soluble oil.

The OH/NH number of the compound was determined analogously with the OH number determination method by acetylation of the compound with acetic anhydride.

35

OH/NH number:

found: 457

calculated: 442

basic N:

found: 3.67%

calculated: 3.78%

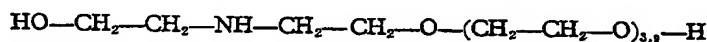
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secondary N:

found: 3.53%

calculated: 3.78%

45 The 3 - β - hydroxyethyl - 2 - phenyloxazolidine used had been prepared as follows: 212 g (2 moles) of freshly distilled benzaldehyde and 210 g (2 moles) diethanolamine were mixed together and fractionally distilled.



are obtained in the form of a water-soluble oil.

75

OH/NH number:

found: 625

calculated: 607

basic N:

found: 5.13%

calculated: 5.06%

80

secondary N:

found: 4.89%

calculated: 5.06%

85 The 3 - β - hydroxyethyl - 2 - isopropylloxazolidine used had been prepared as follows: 144 g (2 moles) isobutyraldehyde and 210 g

326 g (87% of the theory) of 3 - β - hydroxyethyl - 2 - phenyloxazolidine were obtained. b.p. 144°C at 0.35 mm Hg; n_D^{20} : 1.5385.

50

Example 2

48 g (0.3 mole) 3 - β - hydroxyethyl - 2 - isopropylloxazolidine, the preparation of which is described hereinafter, are reacted, with stirring, with 51 g (1.16 moles) ethylene oxide in the presence of 0.3 g of anhydrous sodium hydroxide powder in a nitrogen atmosphere in 4 hours at 150°C. Following the ethoxylation, 300 g of superheated steam are blown through the reaction mixture. The steam is condensed in a distillation cooler. Approximately 70% of the theoretically possible amount of isobutyraldehyde is recovered. The aqueous polyether amine solution is freed from water, first on a rotary evaporator and then by distillation in an oil pump vacuum of 1 to 3 mm Hg until the base of the column has a temperature of 130°C. 79 g of the secondary polyether amine of the formula

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(2 moles) diethanolamine were heated to the boil in 200 ml benzene on a water separator. After 2 hours, about 35 ml had separated. The solution is then distilled. Yield: 290 g (91% of the theory) of 3 - β - hydroxyethyl - 2 - isopropylloxazolidine. b.p. 115°C at 16 mm Hg; n_D^{20} : 1.4602.

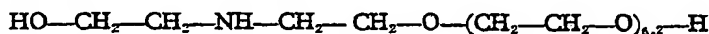
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Example 3

32 g (0.2 mole) 3 - β - hydroxyethyl - 2 - isopropylloxazolidine are reacted at 150°C under the conditions described in Example 2 with 54.4 g (1.24 moles) ethylene oxide in the presence of 0.2 g sodium methylate. After the hydrolysis of the ethoxylation product with 250 g of steam, 73 g of the polyether amine of the formula

95

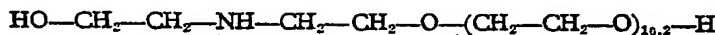
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are obtained in the form of a water-soluble oil.

Example 4

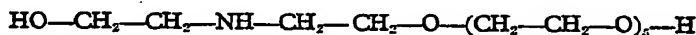
5	OH/NH number:		32 g (0.2 mole) 3 - β - hydroxyethyl - 2 - isopropylloxazolidine are reacted under the conditions described in Example 2 with 90 g (2.05 moles) ethylene oxide in the presence of 0.1 g of sodium. After the hydrolysis of the ethoxylation product with 300 g of steam, 106 g of the secondary polyether amine of the formula	15
	found:	431		
	calculated:	445		
10	basic N:			
	found:	3.57%		
	calculated:	3.71%		
10	secondary N:			
	found:	3.53%		
	calculated:	3.71%		



are obtained in the form of a viscous, water-soluble oil.

Example 5

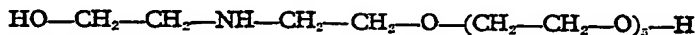
25	OH/NH number:		39 g (0.2 mole) N - β - hydroxyethyl - 2 - oxa - 5 - aza - spiro[4,5]decane, the preparation of which is described hereinafter, are reacted under the conditions described in Example 2 with 44 g (1 mole) ethylene oxide in the presence of 0.5 g of anhydrous sodium hydroxide powder. After hydrolysis of the ethoxylation product with 300 g of steam—the cyclohexanone distilled off with the steam can easily be recovered by extraction with an organic solvent, such as e.g. toluene, from the condensed steam—64 g of the secondary polyether amine of the formula	35
	found:	312		
	calculated:	304		
30	basic N:			
	found:	2.40%		
	calculated:	2.53%		
30	secondary N:			
	found:	2.24%		
	calculated:	2.53%		



50	are obtained in the form of a water-soluble oil.		moles) diethanolamine were heated to the boil in 250 ml toluene on a water separator. After 4 hours, 53 ml of water had separated. The solution was then distilled. Yield: 447 g (80.5% of the theory) of N - β - hydroxyethyl - 2 - oxa - 5 - aza - spiro[4,5]decane. b.p. 145°C at 13 mm Hg; n_D^{20} : 1.4954.	65
	OH/NH number:			
	found:	531		
	calculated:	517		
55	basic N:			
	found:	4.32%		
	calculated:	4.30%		
55	secondary N:			
	found:	4.17%		
	calculated:	4.30%		

Example 6

60	The N - β - hydroxyethyl - 2 - oxa - 5 - aza - spiro[4,5]decane used had been prepared as follows:		35.1 g (0.3 mole) β - hydroxyethylloxazolidine, the preparation of which is described hereinafter, are reacted at 80 to 100°C under the conditions described in Example 2 with 66 g (1.5 moles) ethylene oxide in the presence of 0.3 g boron trifluoride etherate. After hydrolysis of the ethoxylation product with steam, 95 g of the secondary polyether amine of the formula	75
	294 g (3 moles) cyclohexanone and 315 g (3			
60	OH/NH number:			
	found:	531		
	calculated:	517		
55	basic N:			
	found:	4.32%		
	calculated:	4.30%		
55	secondary N:			
	found:	4.17%		
	calculated:	4.30%		



are obtained in the form of a water-soluble oil.

secondary N:		90
found:	3.98%	
calculated:	4.30%	

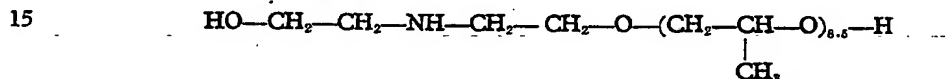
85	OH/NH number:			
	found:	540		
	calculated:	517		
85	basic N:			
	found:	4.17%		
	calculated:	4.30%		
85	The β - hydroxyethylloxazolidine used had been prepared as follows:			
	60 g (2 moles) paraformaldehyde and 210 g (2 moles) diethanolamine were heated to the boil in 200 ml toluene on a water separator.			

After 3 hours, 36 ml of water had separated. The solution was then distilled. Yield: 125 g (79% of the theory) of 3 - β - hydroxyethyl-oxazolidine. b.p.: 115°C at 20 mm Hg; n_D^{20} : 1.4762.

Example 7

32 g (0.2 mole) of 3 - β - hydroxyethyl -

2 - isopropylloxazolidine are reacted at 180°C under the conditions described in Example 2 with 100 g (1.7 moles) propylene oxide in the presence of 0.2 g of sodium. After the hydrolysis of the propoxylation product with 500 g of steam, 112 g of the secondary polyether amine of the formula



are obtained in the form of a water-insoluble viscous oil.

OH/NH number:

found: 294
calculated: 281

basic N:

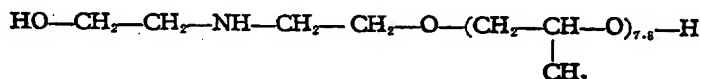
found: 2.40%
calculated: 2.34%

secondary N:

found: 2.23%
calculated: 2.34%

Example 8

39 g (0.2 mole) N - β - hydroxyethyl - 2 - oxa - 5 - aza - spiro[4,5]decane are reacted at 180°C under the conditions described in Example 2 with 50 g (1.55 moles) propylene oxide in the presence of 0.2 g of sodium. After the hydrolysis of the propoxylation product with steam, 108 g of the secondary polyether amine of the formula



are obtained in the form of a water-insoluble viscous oil.

OH/NH number:

found: 320
calculated: 301

basic N:

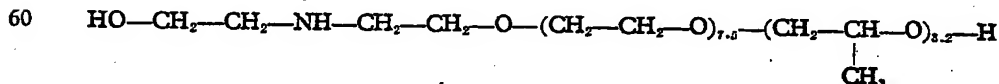
found: 2.43%
calculated: 2.51%

secondary N:

found: 2.43%
calculated: 2.51%

Example 9

32 g (0.2 mole) 3 - β - hydroxyethyl - 2 - n - propylloxazolidine, the preparation of which is described hereinafter, are reacted, in the presence of 0.2 g sodium hydroxide powder and under the conditions described in Example 2, with 66 g (1.5 moles) ethylene oxide at 150°C and subsequently with 38 g (0.65 mole) propylene oxide at 180°C. After the hydrolysis of the alkoxylation product with 500 g of steam, 121 g of the secondary polyether amine of the formula



are obtained in the form of a water-soluble viscous oil.

OH/NH number:

found: 295
calculated: 271

basic N:

found: 2.30%
calculated: 2.25%

secondary N:

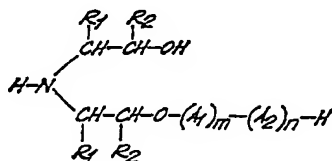
found: 2.12%
calculated: 2.25%

The 3 - β - hydroxyethyl - 2 - n - propyl-oxazolidine used had been prepared as follows:

144 g (2 moles) n-butyraldehyde and 210 g (2 moles) diethanolamine were heated to the boil in 200 ml benzene on a water separator. After 4 hours, 38 ml of water had separated. The solution was then distilled. Yield: 220 g (69% of the theory) of 3 - β - hydroxyethyl - 2 - n - propylloxazolidine. b.p.: 125°C at 13 mm Hg; n_D^{20} : 1.4663.

WHAT WE CLAIM IS:—

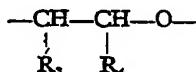
1. Process for the preparation of secondary polyether amines of the formula



in which

R_1 and R_2 , independently of one another, stand for hydrogen, an alkyl or aryl radical,

A_1 and A_2 , independently of one another, denote an oxyalkylene group of the formula

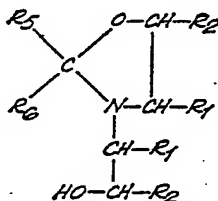


in which

R_3 and R_4 , independently of one another, stand for hydrogen, an alkyl or aryl radical, and

m is a number between 1 and 100 and n is nought or a number between 1 and 100

characterised in that oxazolidines of the formula

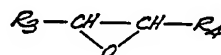


in which

R_1 and R_2 have the meaning stated above, and

R_5 and R_6 , independently of one another, stand for hydrogen, an alkyl or aryl group or, together with the C atom, form a 5- or 6-membered cycloalkane ring

are reacted with alkylene oxides of the formula



in which

R_3 and R_4 have the meaning stated above and the hydroxyalkylation products formed are hydrolysed.

2. A process according to claim 1 in which R_1 , R_2 , R_3 , R_4 , R_5 or R_6 , independently of one another, stand for hydrogen or a C_{1-4} alkyl radical.

3. A process according to claim 1 in which R_1 , R_2 , R_3 , R_4 , R_5 or R_6 , independently of one another, stand for a phenyl radical.

4. A process according to claim 2 in which R_3 or R_4 , independently of one another, stand for chloromethyl.

5. A process according to any one of claims 1 to 4 in which m is 2-30.

6. A process according to any one of claims 1 to 5 in which n is 2-30.

7. A process according to any one of claims 1 to 6 in which the hydroxyalkylation takes place at 40-200°C.

8. A process according to any one of claims 1 to 7 in which the hydroxyalkylation takes place at between 1 and 6 atmospheres pressure.

9. A process according to any one of claims 1 to 8 in which the hydroxyalkylation reaction is conducted in the presence of 0.05-2% by weight of basic catalyst, referred to the weight of the N- β -hydroxyalkyl-oxazolidine to be hydroxyalkylated.

10. A process according to any one of claims 1 to 9 in which the hydrolysis of the oxazolidine hydroxyalkylation products is effected with steam.

11. A process as claimed in claim 1 and substantially as hereinbefore described in any one of Examples 1 to 9.

12. Secondary polyether amines of the formula given in claim 1 when prepared according to the process of any one of claims 1 to 11.

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